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SCIENTIFIC BASIS FOR ULTRA-HIGH BURN-UP NUCLEAR FUELS

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Disclaimer

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Scientific Basis for Ultra-high Burn-up Nuclear Fuels
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Abstract
A key issue on the path to nuclear energy becoming an essential component of the U.S. clean energy strategy is complete burn of the nuclear fuel. We propose research that will enable high-burn-up fuels by establishing the basic science for development and qualification of advanced nuclear fuel that will couple modern computational materials modeling, fabrication, and characterization capabilities with targeted performance-testing experiments using ion-beam facilities. This work will establish the scientific foundation and guide selection of the optimum fuel type for advanced reactor concepts. We expect to experimentally quantify the phase stability and kinetics of phase transformations, inter-diffusion, microstructural evolution, micromechanical properties, and the influence of severe radiation environments on fuel performance and, by the end of the project, develop a validated model for advanced nuclear energy materials under extreme conditions of radiation, temperature, and evolving chemistry. We will provide a science-based path forward to an optimized inert matrix fuel, while contributing to the development of a validated nuclear fuel database. We expect this project will further establish LLNL's credibility in the nuclear energy community.

Mission Relevance
Our approach to advancing the science of advanced nuclear energy fuels aligns well with the Laboratory's energy and national security missions. Development of both advanced fuel cycles and hybrid fusion–fission concepts is inexorably intertwined with the same scientific challenges. This research will extend LLNL capabilities and further enable actinide and high-energy-density science, high-performance computing and simulation, energy manipulation, and capabilities to develop materials on demand.

FY12 Accomplishments and Results
Our *ab initio* work was extended to americium-X (X=neptunium, plutonium, uranium, molybdenum, zirconium), neptunium-Y (Y=molybdenum, zirconium), and uranium-T (T=molybdenum, tantalum, tungsten) and trend towards phase separation or ordering in these series of alloys were drawn. A complete thermodynamic assessment of the plutonium-molybdenum phase diagram with input from ab initio energetics was completed. A new phase in uranium-molybdenum was predicted around the 3:1 composition based on *ab initio* calculations, and a preliminary thermodynamic database molybdenum-plutonium-uranium was developed. Kinetic modeling was applied to uranium-zirconium diffusion couples to optimize geometry for future ion-beam experiments. Our phase-field code was upgraded to include thermal gradient effect and non-periodic boundary conditions, and applied to the effect of coring in alloys and site redistribution in uranium-zirconium in a gradient of temperature. On the experimental side, more samples of uranium-X (X=molybdenum, zirconium) and metal matrix alloys, zirconium-iron-copper, were prepared and characterized at the university of Texas A&M, and we carried out further characterization (x-ray diffraction and transmission electron microscopy) as a function of annealing time. Our studies on actinide alloys showed that TEM is indispensable to reveal features that were not seen before. *E.g.*, in the case of as-cast uranium-zirconium bulk alloys, even at low zirconium composition, the lamellar structure of the decomposition in alpha (orthorhombic U structure) and delta (UZr_2) phases was clearly observed, and characterized. Also, short-range order was observed in quenched body-centered cubic uranium-molybdenum alloy, and further analysis may reveal the existence of a new phase. Finally the very first ion-beam experiment was conducted on bulk uranium-zirconium and post-irradiation examination is still in progress to study microstructural changes caused by irradiation effects.

FY13 Accomplishments and Results
Samples of uranium-molybdenum (U-Mo) and uranium-zirconium (U-Zr), and inert metallic matrix Zr-Fe-Cu alloys were synthetized (3 compositions for each class of alloys) and characterized with X-ray diffraction, transmission electron microscopy (TEM), and differential scanning calorimetry analysis. Sample holders for irradiation experiments were designed and two sets of experiments at two temperatures (450 and 600 C) (with 4 samples per holder) were carried out at the Center for Accelerated Mass Spectrometry. Post examination experiments with XRD and TEM were performed on U-Mo and U-Zr samples. It was shown that in the case of U-Zr, irradiation damage caused a morphology change in the lamellar microstructure with accompanying coarsening and loss of orientation relationship between the a-U and d phases. For U-7 (and

10)wt.% Mo, detailed TEM work revealed a metastable structure that is different from the commonly known high-temperature bcc phase. On the theoretical side, for the first time ab initio calculations of the equilibrium properties for the ternary U-Mo-Zr alloys as function of composition. The study revealed the importance of the contribution of the three-body interactions for describing the Gibss energy of the ternary alloy, an effect that is been largely ignored in past studies. This has consequences on stability and also on kinetics of transformation and microstructure of nuclear fuels. The thermodynamic assessment of additional binary alloys has been extended to Plutonium-X, X=Mo, Tungsten, and also, for the first time to U-Cesium alloys. In this later case, because of enormous atomic size difference between U and Cs, there is a tremendous tendency towards phase separation in this alloy, and we expect the same to be true in the case of U-Strontium alloys. Finally, the LLNL phase-field code has been extended to handle multi-phase microstructures, and applied to U-Zr alloys to study solidification and solid phase-decomposition in the case of U-Zr alloys.

FY14 Accomplishments and Results

Because of the limited funding allocated to the SI in FY14, the work has been limited to mentorship of a postdoctoral Fellow from CEA Valduc, characterization of samples irradiated in FY13, and publication of work under the SI. (1) In the framework of the DOE/NNSA-CEA/DAM cooperation in "Fundamental science supporting stockpile stewardship" (Project P181), a Postdoctoral Fellow joined the team in FY14 to work on the role of daughter products on the stability of Ga-Pu and Al-Pu alloys. Based on an extensive literature search on phase stability properties, and by recasting the bcc phase *ab initio* energetics in the CALPHAD framework, the Pu-U phase diagram has been successfully thermodynamically re-assessed. Then, the Pu-U thermodynamic functions have been combined with the Pu-Ga and U-Ga ones to predict the ternary Pu-U-Ga system. It is worth noting that this system has never been assessed or reported in the literature before. Our predictions show that a small amount of U impacts the δ Pu-Ga phase stability by precipitating the complex η and ζ phases, and therefore may impact swelling and mechanical integrity during aging. Both Pu-U and Pu-U-Ga phase diagrams and property diagrams can be used as guidelines to design experiments that are usually costly, challenging and time-consuming. Indeed, these preliminary diagrams can be used to identify compositions and temperature ranges where maximum information can be obtained to further improve and/or validate the proposed thermodynamic database. By the end of FY14, the thermodynamic properties for the binary Am-U and ternary Am-Pu-U systems have been predicted, and the role of Am on the stability of Pu-U has been evaluated. The study will be extended to the quaternary Am-X-Pu-U (X=Al, Ga) during FY15 of this cooperation. (2) samples of Mo-U have been experimentally characterized with X-rays and TEM, and comparison between non-irradiated and irradiated samples of U-Zr has been carried out.

Overall Accomplishments and Results

During the three-year LDRD-SI, the team has investigated with ab initio aided CALPHAD approach the thermodynamic properties of a series of actinide-based alloys, namely: Am-Pu, Am-U, Mo-Pu, Mo-U, Nb-U, Np-Zr, Pu-U, Ti-U, U-X (X=bcc transition metal), and U-Zr, and the ternary Am-Pu-U, Ga-Pu-U, Mo-Pu-U systems, the quaternary Al-Mo-Si-U system, and the promising inert metal coating Cu-Fe-Zr-X (X=Be, Nb, Ti) alloy. The LLNL phase-field modeling (PFM) code has been updated to account for the CALPHAD data both for the thermodynamic driving force and the kinetic data to study microstructure evolution as a function of quenching rate in Au-Ni and U-Zr alloys. On the experimental side, it was shown that TEM is critical in characterizing nuclear fuels by revealing for the first time the co-existence of a δ phase of UZr_2 with the orthorhombic α phase of U, and the existence of a new phase in Mo-U alloys in the U-rich region where only the bcc phase is supposed to exist. Finally the creation of defects at the LLNL Center for Accelerated Mass Spectrometry (CAMS) by implanting iron ions whose energy was similar to that of a fission fragment emitted by a nuclear power plant in samples of U-Zr alloys has shown that a loss of the materials' well aligned lamellar (or plate-like) microstructure was indicative of a loss of dimensional stability that could impact fuel's performance (and in particular swelling). These studies are highly relevant for several programs at DOE/NNSA and also DOE-NE (in particular the AFCRD, NeUp, and GTRI)

Presentations

43. October 2014: Two Invited presentations at the NuMat 2014 Conference, in Clearwater, FL, October 27-30, 2014:

• P.E.A. Turchi, A. Perron, A.I. Landa, and P.A. Söderlind, "The Role of *Ab Initio* in building up a Physics-based Thermodynamic Database for Nuclear Fuel Materials". (LLNL-ABS-652990).
• C. Guéneau, N. Dupin, T. Besmann, M. Kurata , S. Gossé, P.E.A. Turchi, D. Barber, E. Corcoran, J.-C. Dumas, M. Kaye, R. Hania, B.O. Lee , T. Ogata, R. Kennedy, and S. Massara, "The OECD-NEA Project "Thermodynamics of Advanced Fuels-International Database"

41. October 2014: One oral presentation at the MS&T'2014 Conference, in Pittsburgh, PA, October 12-16, 2014:
• A. Perron, P.E.A. Turchi, A.I. Landa, and P.A. Söderlind, "Thermodynamics of actinide-based alloys: Challenges and Opportunities". (LLNL-ABS-651872; LLNL-PRES-).

40. September 2014: One invited presentation at the Plutonium Futures – The Science 2014 Conference, organized by Scott McCall and Kerri Blobaum, in Las Vegas, NV, September 7-12, 2014:
• A. Perron, P. E. A. Turchi, A.I. Landa, P.A. Söderlind, B. Oudot, B. Ravat, and F. Delaunay, "The Phase stability of actinide alloys: An *ab initio* aided CALPHAD study". (LLNL-ABS-651093; LLNL-PRES-).

39. June 2014: One invited presentation at the 2014 Working Meeting under the International Agreement on Fundamental Science Supporting Stockpile Stewardship, organized by M.N. Kreisler and T. Massard, in Paris France, June 4-5, 2014, presented by Jason Burke (POC):
Aurélien Perron, Patrice Turchi, Alexander Landa, Benoit Oudot, Brice Ravat, and François Delaunay, "CALPHAD Assessment of plutonium-related database – P182". (LLNL-PRES-654695)

38. February 2014: One oral presentation at the 143rd TMS Annual Meeting and Exhibition, in the Hume-Rothery Award Symposium on "Thermodynamics and Kinetics of Engineering Materials", organized by Hans-Peter Seifert, Alan Luo, and Peter Uggowitzer, in San Diego, CA, February 16-20, 2014:
• A. Perron, P.E.A. Turchi, A.I. Landa, P.A. Söderlind, B. Oudot, and F. Delaunay, "Thermodynamic Assessment of Pu-based Alloys: the case of Pu-U and Pu-U-Ga". (LLNL-ABS-640338; LLNL-PRES-649582).

37. February 2014: Two invited presentations at the 143rd TMS Annual Meeting and Exhibition, in the Symposium on "Materials and Fuels for the Current and Advanced Nuclear Reactors III", organized by R. Prabhakaran, D. Keiser, and R. Rebak, in San Diego, CA, February 16-20, 2014:
• Joseph T. McKeown, Sangjoon Ahn, Mark A. Wall, Luke L. Hsiung, Sean McDeavitt, and Patrice E.A. Turchi, "Thermal Stability of Uranium-rich U-Mo Alloys for Advanced Nuclear Fuels". (LLNL-ABS-639984).
• A. Landa, P.E.A. Turchi, and P. Söderlind, "Thermodynamic of U-Mo-Zr Alloys: Application to RERTR Nuclear Fuels". (LLNL-ABS-640336, LLNL-PRES-648622).

36. February 2014: One oral presentation at the 143rd TMS Annual Meeting and Exhibition, in the Symposium on "Accelerated Materials Evaluation for Nuclear Application Utilizing Test Reactors, Ion Beam, and Modeling", organized by P. Hosemann, J.D. Tucker, J.I. Cole, and T.A. Allen, in San Diego, CA, February 16-20, 2014:
Joseph T. McKeown, Sangjoon Ahn, Mark A. Wall, Luke L. Hsiung, Michael Fluss, Scott Tumey, Thomas Brown, Sean McDeavitt, and Patrice E.A. Turchi, "Phase Stability and Evolution of Ion-irradiated Uranium-rich Alloys for Advanced Nuclear Fuels". (LLNL-ABS-639985).

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35. November 2013: One invited presentation at SIAM Annual Meeting
Jean-Luc Fattebert and Patrice E.A. Turchi, "A numerical algorithm for the solution of a phase-field model of polycrystalline alloys – Application to Au-Ni alloys". (LLNL-PRES-646602-DRAFT).

34. October 2013: One invited presentation at the Symposium on "Phase Stability, Diffusion, Kinetics, and their Applications (PSDK-VIII)", at MS&T 2013 Conference and Exhibition, in Montréal, Québec (Canada), October 27-31, 2013, organized by R. Arroyave, R.R. Mohanty, A. Misra, J.C. Lacombe, and M. Gao:
P.E.A. Turchi, A.I. Landa, and P.A. Söderlind, J. McKeown, M. Wall, and L. Hsiung, "Thermodynamics of Actinide-based Nuclear Fuels". (LLNL-ABS-616580; LLNL-PRES-645104).

33. September 2013: One oral presentation at the 2013 LWR Fuel Performance Meeting/Top Fuel, in Charlotte, NC, September 15-23, 2013:
J.T. McKeown, S. Ahn, B. Barnhart, S. Irukuvarghula, M.A. Wall, L.L. Hsiung, S. McDeavitt, and P.E.A. Turchi, "Alloys for Dispersion-type Inert-Matrix Nuclear Fuels". (LLNL-ABS-619032).

32. June 2013: One oral presentation at the American Nuclear Society (ANS) Annual Meeting, in Atlanta, GA, June 16-20, 2013:
J.T. McKeown, S. Ahn, B. Barnhart, S. Irukuvarghula, M. A. Wall, L.L. Hsiung, S. McDeavitt, and P.E.A. Turchi, "Alloy Development for Advanced Inert-Matrix Nuclear Fuels". (LLNL-ABS-609900).

31. May 2013: One invited presentation at the 2013 Working Meeting under the International Agreement on Fundamental Science Supporting Stockpile Stewardship, organized by M. N. Kreisler and T. Massard, in Albuquerque, NM, May 29-31, 2013, presented by Christian Mailhiot (POC):
P.E.A. Turchi, A.I. Landa, A. Perron, and B. Oudot, "Thermodynamic Assessment of Pu-based Alloys". (LLNL-PRES-637073).

30. May 2013: One invited presentation at the International CALPHAD XLI Conference organized by Tomas Gomez-Acebo, in San Sebastian (Spain), May 26-31, 2013:
P.E.A. Turchi, A.I. Landa, P.A. Söderlind, J.-L. Fattebert, V. Lordi, M. Tang, J. McKeown, M. Wall, and L. Hsiung, "Thermodynamics and kinetics of actinide alloys". (LLNL-ABS-616600, LLNL-PRES637045).

29. May 2013: One invited presentation at the NIST Diffusion Workshop organized by Carelyn Campbell, and held in Gaithersburg, MD, May 9-10, 2013:
P.E.A. Turchi, "Acquisition of Diffusion Data from *Ab Initio* – Part II: Representation of *ab initio* results in a database". (LLNL-PRES-636062).

28. April 2013: One oral presentation at the LLNL Seminar CMMD series, April 17, 2013:
J.T. McKeown, "Alloys for Inert-Matrix Advanced Fuels".

27. April 2013: One invited presentation at the 245th ACS National Meeting and Exhibition, in New Orleans (LA), April 7-11, 2013:
A. Landa, P.A. Söderlind, and P.E.A. Turchi, "*Ab initio* study of U-Zr metallic nuclear fuels for fast breeder reactors". (LLNL-ABS-590072; LLNL-PRES-631873).

26. March 2013: One keynote address at the Ringberg Unary Workshop 2013 organized by Drs. Suzana Fries and Tilmann Hickel, in Tegernsee (Germany), March 24-29, 2013:

P.E.A. Turchi, "Thermodynamics of unaries up to the melting point – CALPHAD assessment and beyond". (LLNL-PRES-626324).

25. March 2013: One invited lecture at the Max Planck Institute für Eisenforschung GmbH, Computational Materials Design Department, hosted by Dr. Tilmann Hickel, in Dusseldorf (Germany), March 21, 2013:
P.E.A. Turchi, "Thermodynamics of Alloys: From *ab initio* to phenomenology?". (LLNL-ABS-626673).

24. March 2013: One invited lecture at the Interdisciplinary Center for Advanced Materials Simulations (ICAMS) hosted by Dr. Suzana Fries, in Bochum (Germany), March 19, 2013:
P.E.A. Turchi, "Is tight-binding modeling still relevant?". (LLNL-ABS-616599; LLNL-PRES-626336).

23. March 2013: One oral presentation at the APS March 2013 Meeting, in Baltimore (MD), March 17-22, 2013:
A. Landa, P. Söderlind, and Patrice E.A. Turchi, "Density-functional study of U-TRU-Zr and U-TRU-Mo alloys". (LLNL-ABS-592612).

22. March 2013: One invited presentation at the TMS 2013 Annual Meeting and Exhibition, in San Antonio (TX), March 3-7, 2013:
Joseph T. McKeown, Sandeep Irukuvarghula, Sangjoon Ahn, Mark Wall, Luke L. Hsiung, Sean McDeavitt, and Patrice E. A. Turchi, "Microstructural assessment of U-rich U-Zr alloys for advanced nuclear fuels". (LLNL-ABS-567316).

21. March 2013: One oral presentation at the TMS 2013 Annual Meeting and Exhibition, in San Antonio (TX), March 3-7, 2013:
Brian A. Barnhart, Patrice E.A. Turchi, and Sean M. McDeavitt, "Microstructural assessment of Zr-Fe-Cu alloys as an inert matrix for nuclear fuels". (LLNL-ABS-).

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20. October 2012: One invited lecture at the Japan Atomic Energy Agency (JAEA) hosted by Dr. Masaki Kurata, in Tokai-mura (Japan), October 29-30, 2012:
P.E.A. Turchi, "Advanced sensors for nuclear materials".

19. October 2012: One invited lecture at the Japan Atomic Energy Agency (JAEA) hosted by Dr. Masaki Kurata, in Tokai-mura (Japan), October 29-30, 2012:
P. E. A. Turchi, "The Basic Science of Nuclear Materials at LLNL – Opportunities for Collaboration" (LLNL-ABS-580593; LLNL-PRES-580616).

18. October 2012: One invited presentation at the Nuclear Materials Conference, NuMat 2012, "Materials Development for Nuclear Applications and Extreme Environments", in Osaka (Japan), October 21-25, 2012:
L. Hsiung and P.E.A. Turchi, "Phase Stability and Aging Mechanisms in U-6wt%Nb Alloys" (LLNL-ABS-576572; LLNL-POST-579477).

17. October 2012: One keynote presentation and one presentation at the Nuclear Materials Conference, NuMat 2012, "Materials Development for Nuclear Applications and Extreme Environments", in Osaka (Japan), October 21-25, 2012:
P.E.A. Turchi, A.I. Landa, J.-L. Fattebert, V. Lordi, M. Tang, and P.A. Söderlind, "*Ab Initio* Properties and Thermodynamics of Metallic Nuclear Fuels – A Current Status". (LLNL-ABS-551795; LLNL-PRES-580594).

16. October 2012: One invited presentation at the 6th International Conference on Multiscale Marterials Modeling (MMM 2012), in Singapore, October 15-19, 2012:

P.E.A. Turchi, A.I. Landa, P.A. Söderlind, J.-L. Fattebert, V. Lordi, and M. Tang, "Thermodynamics, Kinetics, and Microstructures of Actinide-based Materials". (LLNL-ABS-580636; LLNL-PRES-580656).

15. October 2012: One invited presentation at the Symposium on "Materials Development for Nuclear Applications and Extreme Environments", at MS&T 2012 Conference and Exhibition, in Pittsburgh (PA), October 07-11, 2012, organized by R. Rebak, K. Fox, R. Prabhakaran, A.A. Csontos, K. Sridharan, B. Lee, E. Hoffman, and E.G. Reddy:
P.E.A. Turchi, A.I. Landa, and P.A. Söderlind, "Thermodynamics of Actinide Alloys: Application to RERTR Nuclear Fuels". (LLNL-ABS-535991; LLNL-PRES-580615).

14. October 2012: One oral presentation at the Symposium on "Materials Development for Nuclear Applications and Extreme Environments", at MS&T 2012 Conference and Exhibition, in Pittsburgh (PA), October 07-11, 2012, organized by R. Rebak, K. Fox, R. Prabhakaran, A.A. Csontos, K. Sridharan, B. Lee, E. Hoffman, and E.G. Reddy:
J.T. McKeown, S. Ahn, S. Irukuvarghula, M. Wall, L.L. Hsiung, S. McDeavitt, P.E.A. Turchi, "Characterization of U-Zr alloys for ultra-high burn-up nuclear fuels". (LLNL-ABS-538571; LLNL-PRES-585333).

13. October 2012: One poster presentation at the session on "Energy Issues", at MS&T 2012 Conference and Exhibition, in Pittsburgh (PA), October 07-11, 2012:
T. Duong, S. Bajaj, A. Landa, P.E.A. Turchi, and R. Arroyave "Density functional study of Uranium-Niobium system". (LLNL-POST-585175).

12. July 2012: One Invited presentation at the International Workshop on "Electron Correlations and Materials Properties of Compounds and Alloys", organized by Igor Abrikosov, Nikitas Gidopoulos, A. Gonis, G.M. Stocks, and P.E.A. Turchi, in Porto Heli (Greece), July 9-13, 2012:
P.E.A. Turchi, A.I. Landa, V. Lordi, Per Söderlind, "Electronic Structure and Thermodynamics of Actinide-based Alloys" (LLNL-PRES-562907).

11. June 2012: One oral presentation at the International CALPHAD XLI Conference organized by Mark Asta and Patrice E.A. Turchi, in Berkeley (CA), June 3-8, 2012:
V. Lordi and P.E.A. Turchi, "Alloy Optimization for Metallic Inert Matrix Fuels" (LLNL-ABS-558416).

10. June 2012: One invited presentation at the International CALPHAD XLI Conference organized by Mark Asta and Patrice E.A. Turchi, in Berkeley (CA), June 3-8, 2012:
A.I. Landa, P. Söderlind, B. Grabowski, P.E.A. Turchi, A.V. Ruban, and L. Vitos, "Ab Initio Study of Advanced Metallic Nuclear Fuels for Fast Breeder Reactors" (LLNL-ABS-541312).

9. May 2012: One invited presentation at the "2012 NIST Diffusion Workshop" in Gaithersburg (MD), May 3-5, 2012, organized by C. Campbell:
P.E.A. Turchi, "Pseudo-potential method and its limitations". (LLNL-PRES-553992).

8. April 2012: One invited presentation at Symposium Y on "Actinides – Basic Science, Applications, and Technology", at the Spring MRS Meeting in San Francisco, April 9-13, 2012,, organized by Sung Woo Yu, Tomasz Durakiewicz, Corwin Booth, Peter C. Burns, and Roberto Caciuffo:

A. Landa, P. Söderlind, B. Grabowski, P.E.A. Turchi, A.V. Ruban, and L. Vitos, "Ab initio study of advanced metallic nuclear fuels for fast breeder reactors". (LLNL-ABS-508933)

7. March 2012: One oral presentation at the Symposium on "Refractory Metals 2012", at TMS 2012 Annual Meeting and Exhibition, in Orlando (FL), March 11-15, 2012, organized by E. Taleff, T. Leonhardt, R. DeLucas, and G. Rozak:
P.E.A. Turchi, V. Drchal, and J. Kudrnovsky, "Ab initio phase diagrams of bcc-based transition metal alloys – Consequences on properties". (LLNL-PRES-535891)

6. March 2012: One oral presentation at the Symposium on "Computational Thermodynamics and Kinetics: Cluster Expansion, Kinetic Monte Carlo, and First-principles", at TMS 2012 Annual Meeting and Exhibition, in Orlando (FL), March 11-15, 2012, organized by Z.-K. Liu, M. Asta, J. Warren, Y. Wang, R. Arroyave, and Yu Wang:
A. I. Landa, P. Söderlind, P.E.A. Turchi, A. Ruban, and L. Vitos: "Ab initio study of advanced metallic nuclear fuels for fast breeder reactors". (Abs: LLNL-ABS-490670, Pres: LLNL-PRES-535793)

5. March 2012: Two oral presentations at the Symposium on "Materials for the Current and Advanced Nuclear Reactors", at TMS 2012 Annual Meeting and Exhibition, in Orlando (FL), March 11-15, 2012, organized by R. Prabhakaran, D. Keiser, and R. Rebak:
• P.E.A. Turchi, A.I. Landa, and P. Söderlind: "Thermodynamic properties of complex actinide alloys". (LLNL-PRES-535971)
• V. Lordi, M. Wall, L. Hsiung, R. Foreman, and P.E. . Turchi, "Inter-diffusion kinetics in U-Zr". (Abs: LLNL-ABS-491639, Pres: LLNL-PRES-540511)
• Session Chair for the Thursday session on "Materials for the Current and Advanced Nuclear Reactors: Modeling II", March 15, 2012.

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3. November 2011: Two invited lectures at Idaho National Laboratory, Idaho Falls (ID), November 16, 2011, hosted by Dr. Rory Kennedy, head of the Metal Fuel Development Technical Area
P.E.A. Turchi, "The Science of advanced nuclear fuels: Opportunities for collaboration".
Luke Hsiung

2. November 2011: One invited lecture at the Materials Science Program seminar series at the University of Wisconsin-Madison (WI), November 10, 2011, hosted by Prof. J. H. Perepezko
P.E.A. Turchi, "Thermodynamics of alloys: The road from ab initio to phenomenology".

1. October 2011: One invited presentation at the Symposium on "Phase Stability, Kinetics, and their Applications (PSDK-VI)" at MS&T'11 in Columbus (OH), October 16-20, 2011, organized by J. C. Lacombe, Y. H. Sohn, U. Kattner, R. Arroyave, A. Misra, and J. Morral:
P.E.A. Turchi, A. I. Landa, and P. Söderlind, "Thermodynamic database validation and the role of ab initio".

Publications and Reports

• Saurabh Bajaj, Cem Sevik, Tair Cagin, Andres Garay, P.E.A. Turchi, and Raymundo Arroyave, "On the Limitations of the DFT+U Approach to Energetics of Actinides", Computational Materials Science 59, 48-56 (2012).

• A. Landa, P. Söderlind, P.E.A. Turchi, L. Vitos, O.E. Peil, and A.V. Ruban , "Density functional study of bcc Pu-U, Pu-Np, Pu-Am, and Pu-Cm Alloys", J. of Nucl. Mater. **408**, 61-66 (2011). (LLNL-JRNL-441353).

• A. Landa, P. Söderlind, B. Grabowski, P.E.A. Turchi, A. V. Ruban, and L. Vitos, "Ab Initio Study of Advanced Metallic Nuclear Fuels for Fast Breeder Reactors", published in the MRS Proceedings on "Actinides – Basic Science, Applications, and Technology", 14 pages (LLNL-CONF-552336).

• J. McKeown, M. Wall, L. Hsiung, and P.E.A. Turchi, Report on "Characterization of U-10wt% Zr Alloy", 19 pages (March 1, 2012). (LLNL-TR-534973).

• P.E.A. Turchi and A.I. Landa, Report on "Thermodynamic Database – Lower Length Scale, Part I: Thermodynamic Assessment of the Ternary Alloy System Mo-Pu-U", 31 pages (April 26, 2012). (LLNL-TR-553775).

• S.M. Mc Deavitt, B. Barnhart, and I. Sandeep, "Fuel Manufacturing Development for an Advanced Composite Nuclear Fuel – Status Report", 20 pages (February 25, 2012, and August, 10, 2012).

• P.E.A. Turchi and A.I. Landa, Report on "Thermodynamic Database – Lower Length Scale, Part II: Thermodynamic Assessment of Al-Mo-Si-U", 41 pages (September 26, 2012). (LLNL-TR-603054).

• A. Landa, P. Söderlind, and P.E.A. Turchi, "Density-functional study of bcc U-Mo, Np-Mo, Pu-Mo, and Am-Mo alloys, J. of Nucl. Mater. **434**, 31-37 (2013). (LLNL-JRNL-577773).

• J. T. McKeown, S. Irukuvarghula, S. Ahn, M. A. Wall, L. L. Hsiung, S. McDeavitt, and P.E.A. Turchi, "Coexistence of the α and δ phases in an as-cast uranium-rich U–Zr alloy", J. of Nucl. Mater. **436**, 100-104 (2013). (LLNL-JRNL-579942).

• A.I. Landa, P.A. Söderlind, and P.E.A. Turchi, "Research quashes the conventional picture of some thermodynamic functions", LLNL NewsLine, 04/10/2013. https://webcenter.llnl.gov/myllnl/faces/oracle/webcenter/portalapp/pages/top-story-wrapper.jspx?articleId=27181

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Accomplishments

Because of the limited funding allocated to the SI in FY14, the work has been limited to mentorship of a postdoctoral Fellow from CEA Valduc, characterization of samples irradiated in FY13, and publication of work under the SI. (1) In the framework of the DOE/NNSA-CEA/DAM cooperation in "Fundamental science supporting stockpile stewardship" (Project P181), a Postdoctoral Fellow joined the team in FY14 to work on the role of daughter products on the stability of Ga-Pu and Al-Pu alloys. Based on an extensive literature search on phase stability properties, and by recasting the bcc phase *ab initio* energetics in the CALPHAD framework, the Pu-U phase diagram has been successfully thermodynamically re-assessed. Then, the Pu-U thermodynamic functions have been combined with the Pu-Ga and U-Ga ones to predict the ternary Pu-U-Ga system. It is worth noting that this system has never been assessed or reported in the literature before. Our predictions show that a small amount of U impacts the δ Pu-Ga phase stability by precipitating the complex η and ζ phases, and therefore may impact swelling and mechanical integrity during aging. Both Pu-U and Pu-U-Ga phase diagrams and property diagrams can be used as guidelines to design experiments that are usually costly, challenging and time-consuming. Indeed, these preliminary diagrams can be used to identify compositions and temperature ranges where maximum information can be obtained to further improve and/or validate the proposed thermodynamic database. By the end of FY14, the thermodynamic properties for the binary Am-U and ternary Am-Pu-U systems have been predicted, and the role of Am on the stability of Pu-U has been evaluated. The study will be extended to the quaternary Am-X-Pu-U (X=Al, Ga) during FY15 of this cooperation. (2) samples of Mo-U have been experimentally characterized with X-rays and TEM, and comparison between non-irradiated and irradiated samples of U-Zr has been carried out.

Project Summary

During the three-year LDRD-SI, the team has investigated with ab initio aided CALPHAD approach the thermodynamic properties of a series of actinide-based alloys, namely: Am-Pu, Am-U, Mo-Pu, Mo-U, Nb-U, Np-Zr, Pu-U, Ti-U, U-X (X=bcc transition metal), and U-Zr, and the ternary Am-Pu-U, Ga-Pu-U, Mo-Pu-U systems, the quaternary Al-Mo-Si-U system, and the promising inert metal coating Cu-Fe-Zr-X (X=Be, Nb, Ti) alloy. The LLNL phase-field modeling (PFM) code has been updated to account for the CALPHAD data both for the thermodynamic driving force and the kinetic data to study microstructure evolution as a function of quenching rate in Au-Ni and U-Zr alloys. On the experimental side, it was shown that TEM is critical in characterizing nuclear fuels by revealing for the first time the co-existence of a d phase of UZr_2 with the orthorhombic a phase of U, and the existence of a new phase in Mo-U alloys in the U-rich region where only the bcc phase is supposed to exist. Finally the creation of defects at the LLNL Center for Accelerated Mass Spectrometry (CAMS) by implanting iron ions whose energy was similar to that of a fission fragment emitted by a nuclear power plant in samples of U-Zr alloys has shown that a loss of the materials' well aligned lamellar (or plate-like) microstructure was indicative of a loss of dimensional stability that could impact fuel's performance (and in particular swelling). These studies are highly relevant for several programs at DOE/NNSA and also DOE-NE (in particular the AFCRD, NeUp, and GTRI)

Next Steps

This project has clearly demonstrated the relevance of our unique capabilities in terms of modeling and experiments, especially our irradiation facility for actinide alloys. This work is contributing since March 2013 to an OECD-NEA project on "Thermodynamics of Advanced Fuel-International Database (TAF-ID)". We are also exploring collaboration with KAERI (South Korea) that expressed an interest in our approach to the basic science of ultra-high burn-up advanced nuclear fuels, especially the inert-matrix fuel concept originally proposed by the Bochvar Institute (Russia), for next generation nuclear reactors.

ADC: Scott McCall

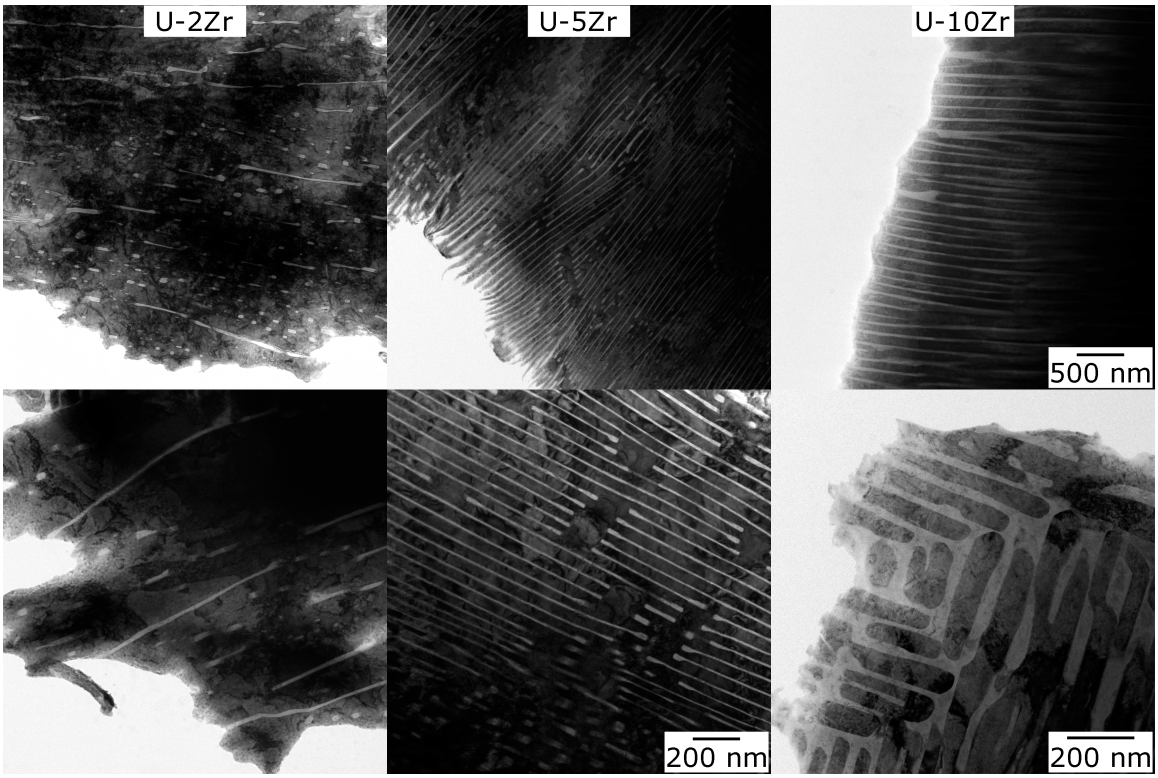

Fig. 1. (a) Bright-field TEM images showing the morphology of the as-cast U-Zr alloys at all three compositions. Scale bars and composition labels apply to all images in rows and columns, respectively.

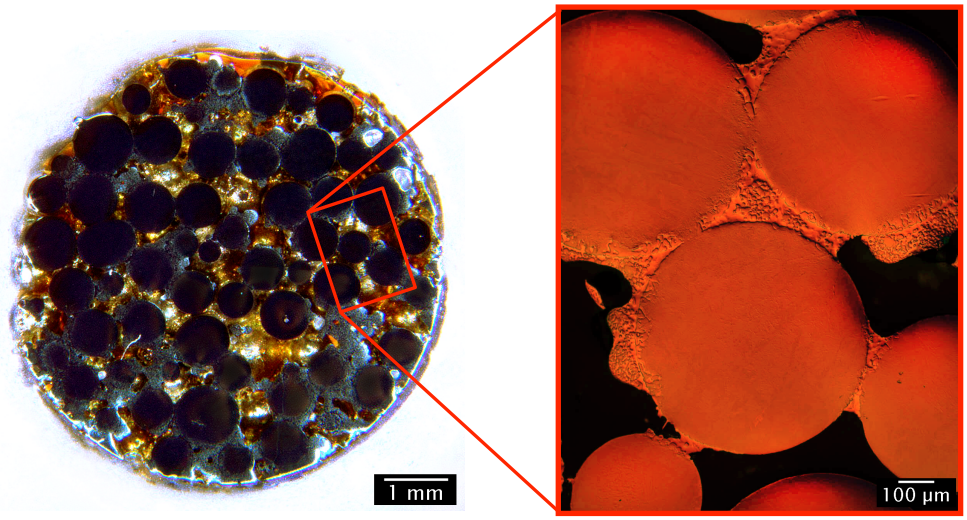

Fig. 2. Large Zr granules of fuel surrogate coated by a metal matrix of Zr-6.2Fe-3.0Nb-2.8Be (in wt.%) with volume fractions of 63% Zr granules, 13% of Zr matrix, and 24% of porous region.